New Transition-Metal-Catalyzed Annulations for Synthesis of Organic Dyes and OFET Semiconductors

博士論文

New Transition-Metal-Catalyzed Annulations for Synthesis of Organic Dyes and OFET Semiconductors

（新規遷移金属触媒環化反応を用いた有機色素および OFET 半導体材料の合成）

趙　健

平成２５年

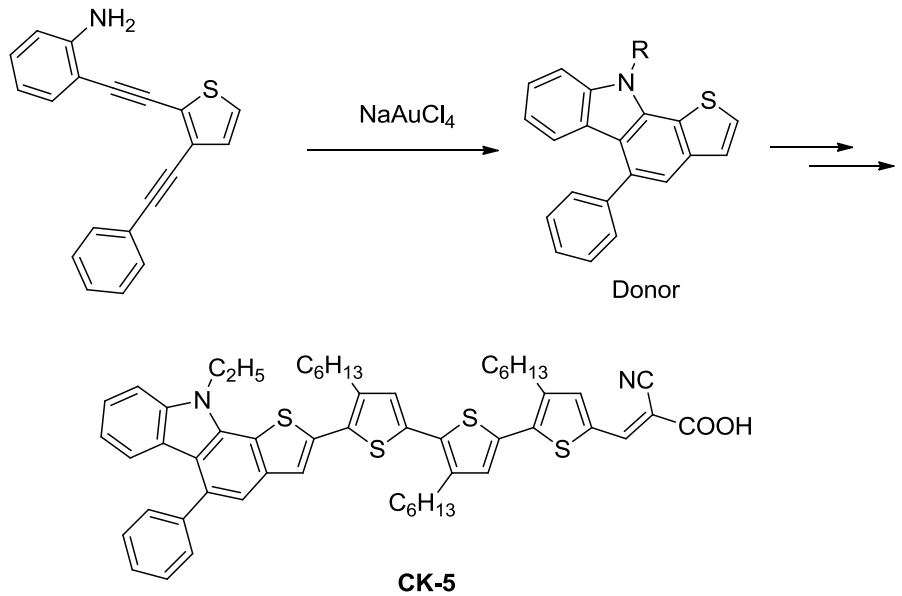
論　文　目　次

Introduction

Polycyclic aromatic compounds have attracted increasing interests as organic semiconductors for various electronic device applications, such as organic field effect transistors (OFETs), organic light emitting diodes (OLEDs), and organic photovoltaics (OPVs). Though many synthetic methods have been developed to synthesize these skeletons, new shortcuts are desirable for the construction of complex and interesting polycyclic aromatic compounds by transitional metal catalysts. In this context, I reported the new cascade annulations by gold or palladium catalysts. The corresponding products were further applied to the synthesis of new organic dyes as electron donor moieties for dye-sensitized solar cells (DSCs) and OFET materials.

1) Au-catalyzed double cascade cyclization for construction of thienocarbazoles: application to the synthesis of molecular dye for dye-sensitized solar cells

In the continuation of our interest in Au-catalyzed transformations and their application in the synthesis of new donor-acceptor-donor (D-A-D) materials, I here reported a new Au-catalyzed double cascade cyclization for construction of thienocarbazoles, and application of the framework as a donor moiety in donor-π-acceptor (D-π-A) organic dyes. DSC based on the new organic dye **CK-5** produced a high power conversion efficiency of 7.42%.

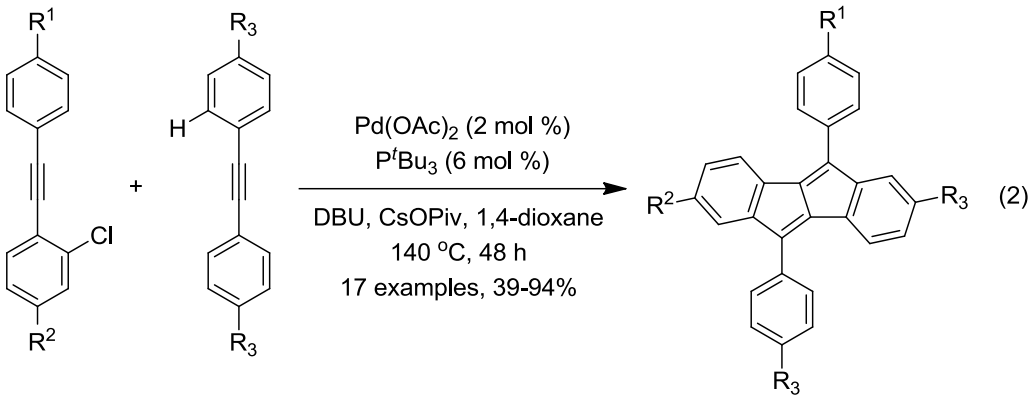


CK-5
Solar Eff. = 7.42%

2) Pd-Catalyzed Cascade Crossover-Annulation of *o*-Alkynylarylhalides and Diarylacetylenes Leading to Dibenzo[*a*,*e*]pentalenes

A novel and selective Pd-catalyzed cascade crossover-annulation of *o*-alkynylarylhalides and diarylacetylenes for the synthesis of dibenzo[a,e]pentalenes has been reported. Various arylacetylenes with a wide range of functional groups were tolerated, producing the corresponding multisubstituted

dibenzopentalenes with the different substituents on the aromatic rings in good to high yields under the optimized reaction conditions. The reaction proceeds through a Pd-catalyzed cascade carbopalladation and C−H activation. The use of the combined DBU and CsOPiv bases is crucial for the successful implementation of the present cross-annulation.



3) Pd-Catalyzed Heck-Type Cascade Cyclizaiton of *o*-Alkynylarylhalides and Dialkylacetylenes

A novel and selective Pd-catalyzed cascade crossover-annulation of *o*-alkynylarylhalides and dialkylacetylenes for the synthesis of dihydrocyclopenta[a]indene has been reported. Various *o*-alkynylarylhalides and dialkylacetylenes with a wide range of functional groups were tolerated, producing the corresponding dihydrocyclopenta[a]indene with the different substituents on the aromatic rings in good to high yields under the optimized reaction conditions. The reaction proceeds through a Pd-catalyzed multi Heck-type cascade pathways.